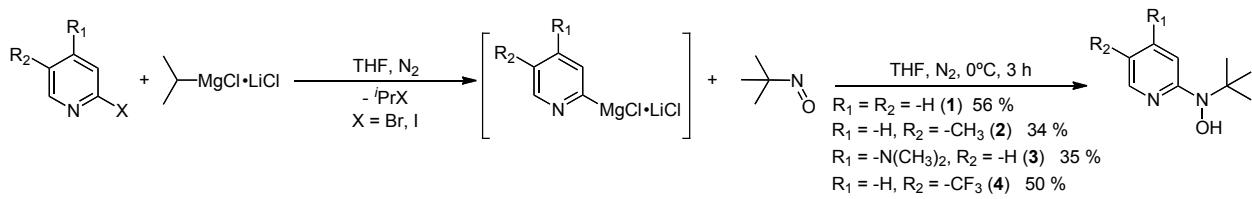


Project Title	A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall		
Recipient Organization and Street Address	Trustees of the University of Pennsylvania 3451 Walnut Street Philadelphia, PA 19104		
Principle Investigator: Eric J. Schelter	Reporting time span (final): 5/14/11 – 8/1/16	DOE Award Number: DE-SC0006518	Unexpended Funds: \$ 0

Technical Results Summary. The project DE-SC0006518 resulted in 32 publications and one patent. We developed and studied the coordination chemistry of rare earth metal (RE = La–Lu, Sc and Y) cations with redox active hydroxylamine ligands, expanded the chemistry of cerium with variable ligands and studied its complexes using experiment and computational chemistry. We disclosed the development of the tripodal hydroxylamine ligand, $[(2\text{-}^t\text{BuNO})\text{C}_6\text{H}_4\text{CH}_2]_3\text{N}]^{3-}$ (TriNOx^{3-}).^[1] The essential feature of the TriNOx^{3-} ligand was its three hydroxylaminato arms that provided an open, but restricted, coordination site. In addition to primary coordination of RE cations, this ligand system induced a self-association equilibrium between monomeric $\text{RE}(\text{TriNOx})\text{THF}$ /dimeric $[\text{RE}(\text{TriNOx})]_2$ species for $\text{RE} = \text{La–Sm}$. An estimated 10^{11} -fold decrease in K_{dimer} was observed across the series, which showed the sensitivity of the self-association process to small changes in RE^{3+} radius. The organic solubilities of the $[\text{RE}(\text{TriNOx})]_2$ complexes were larger than the $\text{RE}(\text{TriNOx})\text{THF}$ ones. Washing solutions of mixed RE complexes with the appropriate solvents afforded purification of individual RE complexes through leaching. On the basis of these observations, a separations method for early/late RE mixtures based on the TriNOx^{3-} system was developed. Nd/Dy ($S = 359$) and Eu/Y ($S = 28.2$) were achieved. These mixtures were targeted because of their critical components of permanent magnets and phosphor materials in fluorescent light bulbs. Subsequently, we demonstrated that other pairs of early and late RE cations can be separated, with $S_{\text{RE1/RE2}}$ approaching 2000.^[2] Overall, new coordination and redox chemistry was demonstrated and applied to the development of a new method for targeted separations of pairs of RE cation, particularly those used widely in technology. The new separations method was patented and is expected to contribute to recycling of RE containing consumer materials.

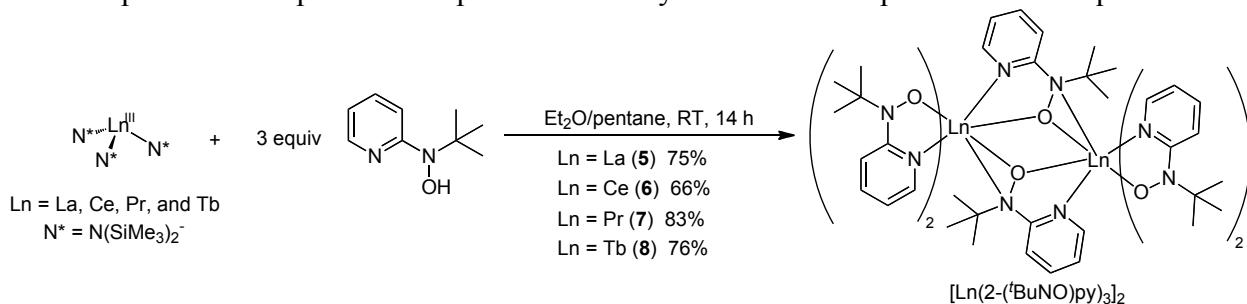
Synthesis and Characterization of Hydroxylamine Ligands and Rare Earth-Hydroxylamine Complexes. Our hypothesis for this Objective was that hydroxylamines ($\text{RR}'\text{NOH}$) and other chalcogenide donor ligands would function as strong, multi-haptic donors for RE cations.^[3, 4] And that the resulting complex properties: redox and solution equilibria, could be leveraged for separations chemistry. In this context we discovered new syntheses of pyridyl-appended hydroxylamine ligands.^[5] For example, ligands **1–4** are now reliably prepared in 35–56 % yields (Scheme 1). The preparation of compound **1** has been simplified and rendered safer by eliminating the need for alkylolithium reagents. We have also shown that this ligand framework can be modulated; methyl-, dimethyl-amino-, and trifluoromethyl- analogs have been prepared (Scheme 1). We have characterized **1–4** electrochemically to determine their electron affinities.



Scheme 1. Synthesis of pyridyl-hydroxylamine ligands **1–4**.

Metal Hydroxylamine Complex Syntheses and Characterization. Ligands **1–3** were used to prepare metal complexes with La, Ce, Pr and Tb (**5–8**, Scheme 2). The resulting complexes are dimeric and have been fully characterized using X-ray crystallography.[6] These data show that hydroxyl-amine ligands are favorable donors for the formation of complexes with trivalent rare earth ions.

Following the synthesis of the dimeric RE^{III} metal complexes, the oxidation chemistry of the Ce^{III} complex **6** was explored. Complex **6** is trivially oxidized in the presence of an equivalent of



Scheme 2. Synthesis of trivalent rare earth complexes using the pyridyl-hydroxylamine ligand **1**.

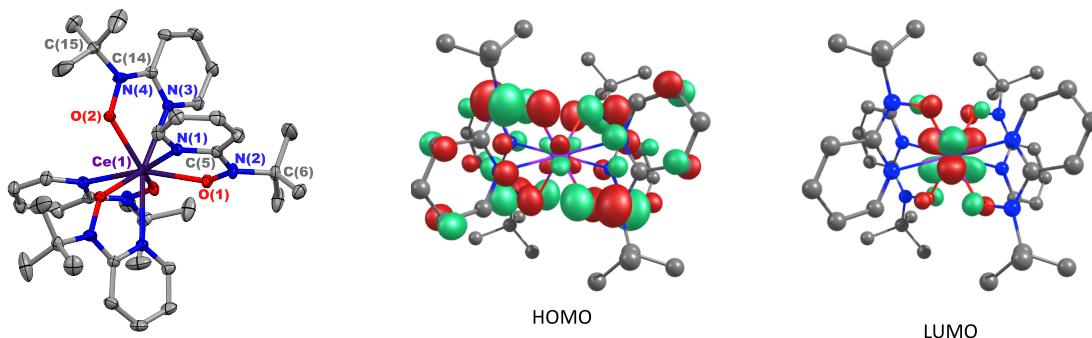


Figure 1. A 30 % probability thermal ellipsoid plot for the crystal structure of complex **9** (left) and results of the hybrid DFT calculations on **9** (HOMO, center and LUMO (right). The HOMO-LUMO gap of **9**, DE = 2.65 eV.

the radical nitroxide form of ligand **1** to form the formally Ce^{IV} complex Ce[2-(¹BuNO)py]₄ (**9**), (Figure 1, left). Consistent with its ease of chemical oxidation, the electrochemical data for **9** collect in THF indicate a reduction feature at $E_{pa} = -1.9$ V versus ferrocene; *complex 9 is the most stable Ce^{IV} complex known.*[6]

B3LYP hybrid DFT calculations were performed on **9** and determined the closed shell Ce^{IV} configuration is the most stable. It should be noted that intermediate valence cannot be detected using DFT, but the DFT results provide an initial assessment of the molecular orbitals responsible for possible intermediate valence effects in these complexes. In fact, good agreement was found

between the LMCT band, $\sim 19,000\text{ cm}^{-1}$, and the calculated HOMO-LUMO gap, which spans about $\sim 20,000\text{ cm}^{-1}$ for **9**.

The results of this work are important for discovering new bonding modes in fundamental f-element chemistry and for potentially for development of improved extractants in solvent extraction technology. Another finding of the project was that the dimeric complexes such as **6** are insoluble in organic solvents while the oxidized congener **9** is soluble (Scheme 4) which potentially enables simplified separations tied to redox chemistry.

Based on the chemistry developed for the hydroxylamine ligand syntheses (Scheme 1), the synthesis, and characterization of six pyridyl-nitroxide Ce^{III} complexes and six Ce^{IV} complexes has been achieved.[7] Characterization of the full series of complexes was made using solution electrochemistry experiments, L_{III} edge X-ray absorption spectroscopy, and density functional theory. In particular, electron donating groups appended to the pyridyl groups have been found to shift the $\text{Ce}(\text{III/IV})$ redox wave to more than -2.0 V versus ferrocene (Figure 2).

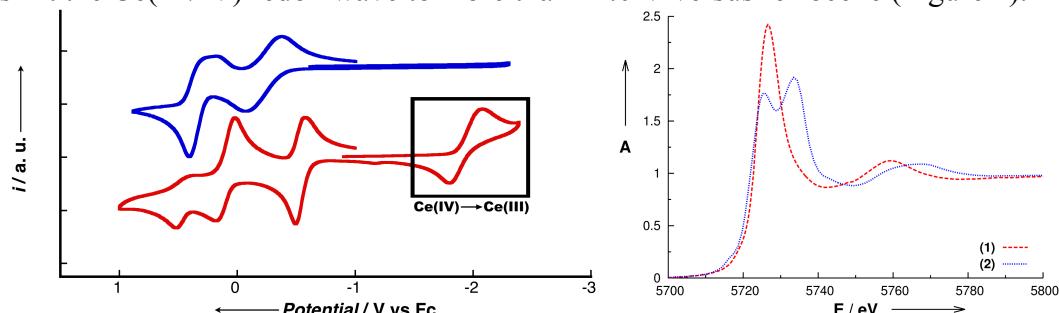


Figure 2. Left: solution electrochemistry of the parent pyridyl appended hydroxylamine ligand (blue trace) and $\text{Ce}(\text{IV})$ complex recorded in CH_2Cl_2 . Right: cerium L_{III} edge X-ray absorption spectra for the parent cerium(III) and cerium(IV) pyridyl-appended hydroxylamine complexes.

Furthermore, the XAS data confirmed the compounds are bona fide Ce^{IV} complexes. The physicochemical data suggest they are the most strongly thermodynamically stabilized Ce^{IV} compounds that have been reported. In order to understand the origin of this unprecedented stabilization, DFT calculations were performed on the compounds (Figure 3).

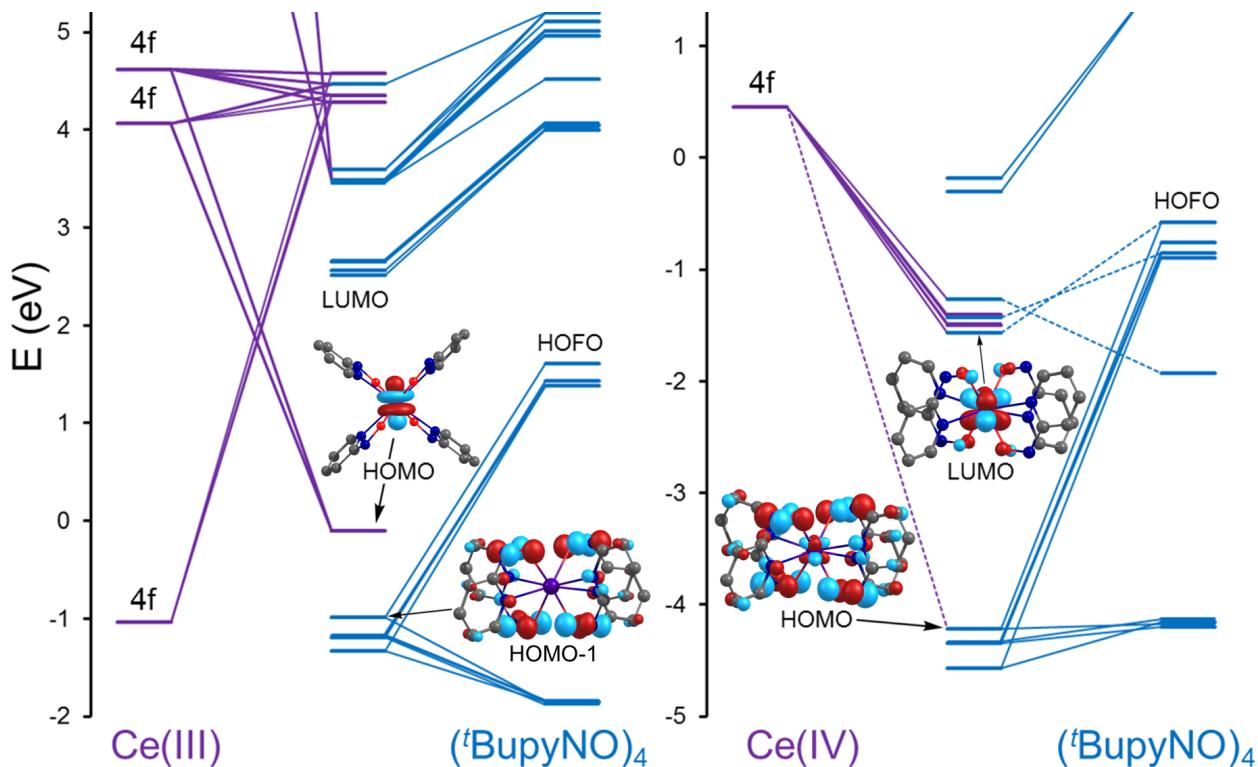


Figure 3. Fragment molecular orbital correlation diagrams for $\text{Ce}[2-(\text{t-BuNO})\text{py}]_4$ (right) and its anion (left). A small but important covalent 4f orbital contribution to bonding is found in $\text{Ce}[2-(\text{t-BuNO})\text{py}]_4$ but not in its anion.

The DFT results revealed a critical, partial covalent contribution from the nitroxide ligand field to the Ce^{IV} cation that serves to strongly stabilize the high oxidation state metal cation.

Multi-dentate nitroxide ligands and their coordination chemistry with the Rare Earth Elements.[8, 9] We hypothesized that tethering three nitroxide arms to a central amine ligand would similarly stabilize the tetravalent oxidation state of a cerium (or other lanthanides) ion but reduce the tendency for ligand redistribution upon oxidation. A tripodal ligand framework was expected to provide a binding pocket for controlled coordination chemistry within an open coordination site.[10] We achieved the synthesis of a tripodal nitroxide ligand: $((2-\text{t-BuNOH})\text{C}_6\text{H}_4\text{CH}_2)_3\text{N}$ (H_3TriNOx), its coordination to a central cerium cation to form the complex: $\text{Ce}(\text{THF})(\text{TriNOx})$ (Figure 4). The $\text{Ce}(\text{THF})(\text{TriNOx})$ complex has a strongly stabilized Ce oxidation at -0.93 V versus ferrocene. We have chemically oxidized the complex to form the stable cerium(IV) compound: $\text{CeCl}(\text{TriNOx})$. These results set the stage for the study of other lanthanides in this strongly stabilizing, multi-dentate framework (see below).

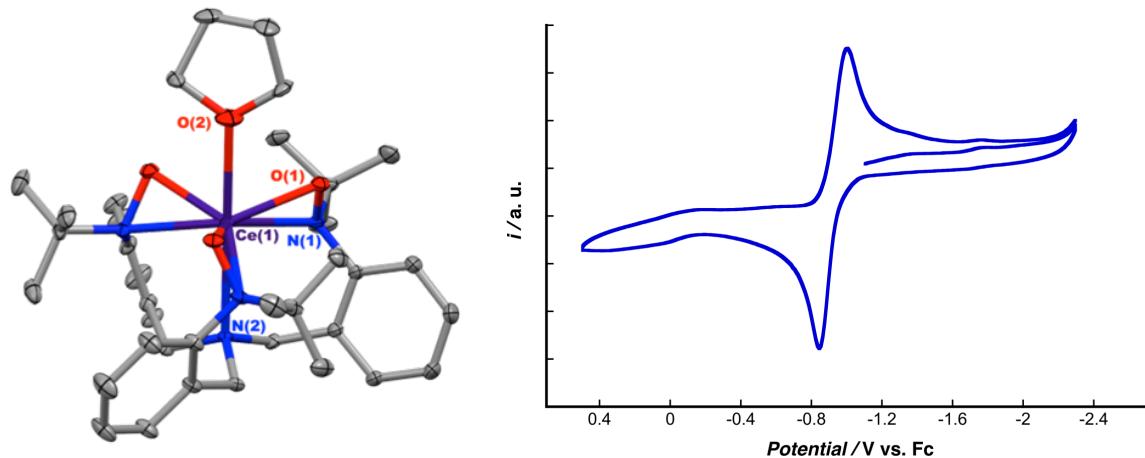


Figure 4. Crystal structure of Ce(THF)(TriNOx) (left) and cyclic voltammogram of Ce(THF)(TriNOx) in CH_2Cl_2 (right).

Isolation and characterization of a cerium(IV) hydroxamate complex. In the context of froth filtration beneficiation of rare earths ores, beneficiation by froth floatation is the first separations unit operation for claiming rare earth metals from ores. Crushed rare earth mineral (e.g. baestnesite) solids are separated from gangue materials through surface chemistry of organic chemical ‘collectors,’ such as hydroxamates, with bound rare earth cations. Our characterization of a cerium hydroxamate complex showed a strong thermodynamic preference for the cerium(IV) state.[11] These results indicated that engineering models of froth floatation must include redox chemistry, which we expect will contribute to increased efficiency in this critical minerals treatment process.

An experimental/DFT-predicted correlation of the cerium redox properties for 15 metal complexes has been achieved (Figure 5). Starting from crystal structures, DFT was applied to compute absolute energies for the compounds in both oxidized and reduced forms, using solvent continuum models. Correlating the energy differences from these computations with the experimentally measured $E_{1/2}$ values from electrochemistry produced an excellent correlation with a range of more than 2.5 V, from highly reducing Ce(III) complexes developed by our group to the strongly oxidizing $[^7\text{Bu}_4\text{N}]_2[\text{Ce}(\text{NO}_3)_6]$. In this context, we also reviewed the literature on cerium redox properties to compare with our results.[12] As part of a larger effort in developing f-element redox chemistry,[13, 14] we leveraged our knowledge to isolate new examples of cerium complexes with unprecedented bonds[15] and unusual (electronic) structures,[16, 17] expanded the literature of strongly stabilized Ce(IV) complexes,[18-20] supported related DOE projects on f-element electronic structure,[21-23] and new information on the interaction of Lewis acids with redox active ligands.[24-26] With

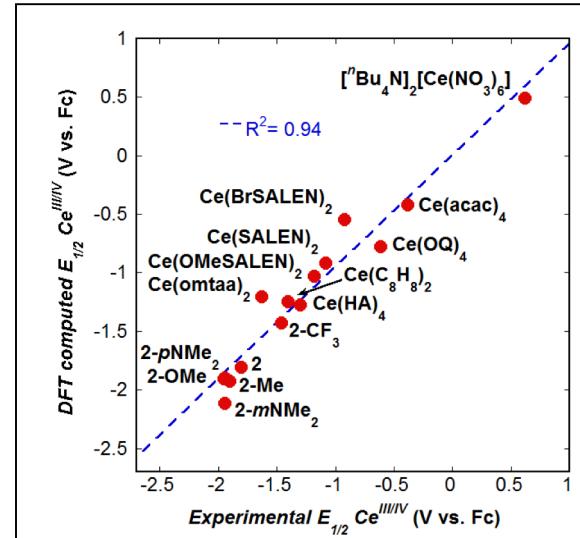


Figure 5. Correlation between experimental and DFT computed redox potentials for 15 cerium complexes.

the first successful application of DFT to predict lanthanide redox properties, we expect this approach will find broad application in separations, including the design of chemical systems for lanthanide/actinide separations.

Organic-Fluorine and their Applications in Shaping F-element Coordination Spheres. An offshoot of our work with cerium redox chemistry was the development of methods in controlling metal coordination sphere structures and geometries,[27] and reactivities,[28] namely through leveraging organo-fluorophilic interactions. These results afforded isolation of complexes in new and unusual coordination geometries,[29] and evaluation of the solution thermodynamic and electronic parameters of such fluorine-metal interactions and their ensembles.[30, 31] These results provide new methods to control the structure of metal complexes, and potentially their redox properties and separations.

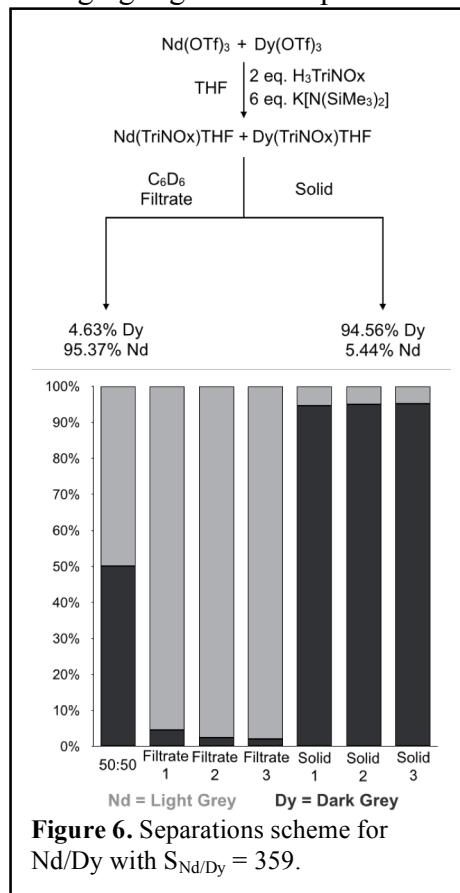


Figure 6. Separations scheme for Nd/Dy with $S_{\text{Nd/Dy}} = 359$.

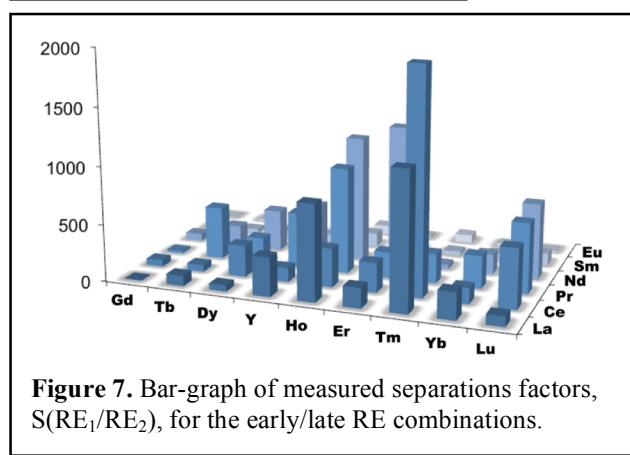


Figure 7. Bar-graph of measured separations factors, $S(\text{RE}_1/\text{RE}_2)$, for the early/late RE combinations.

Discovery of a New Methods for Chemically Separating Rare Earth Elements for Use in Recycling, namely neodymium and dysprosium from magnetic materials. Recycling of consumer materials is a promising new source of rare earths. To incentivize recycling there is a clear need for operationally simple methods for targeted separations of mixtures of rare earth metal salts. In working toward achieving this goal we developed coordination chemistry for multi-dentate nitroxide ligands.[8, 9] Metal complexes of a tripodal nitroxide ligand $[(2'\text{-BuNO})\text{C}_6\text{H}_4\text{CH}_2]_3\text{N}]^{3-}$ (TriNOx^{3-}), feature a size-sensitive aperture formed of its three $\eta_2\text{-}(\text{N},\text{O})$ ligand arms.[10] Exposure of metal cations in the aperture induces a self-associative equilibrium comprising $[\text{M}(\text{TriNOx})\text{thf}]/[\text{M}(\text{TriNOx})]_2$ (M = rare earth metal). Differences in the equilibrium constants (K_{eq}) for early and late metals enables simple Nd/Dy separations through leaching with a separation ratio $S_{\text{Nd/Dy}}=359$, which is comparable or better than separations factors achieved by industry using liquid-liquid extraction for those ions. Subsequently, we showed that other pairs of early and late RE cations can be separated, with $S_{\text{RE1/RE2}}$ approaching 2000. Overall, new coordination and redox chemistry was demonstrated and applied to the development of a new method for targeted separations of pairs of RE cation, particularly those used widely in technology. The new separations method was patented and is expected to contribute to recycling of RE containing consumer materials (Figure 7).

An Expanded Knowledge of the Physicochemical Characteristics of Expanding the Chemistry of Cerium(IV) Complexes. The trivalent cerium compound $K[Ce[N(SiHMe_2)_2]_4]$ was synthesized and oxidized, providing a convenient route to the cerium(IV) compound $Ce[N(SiHMe_2)_2]_4$. $Ce[N(SiHMe_2)_2]_4$ underwent protonolysis with alcohols to yield $Ce(O'Bu)_4(py)_2$, $Ce(Odpp)_4$, and $Ce_2(OCH_2C_6R_5)_8(THF)_2$ ($R = Me, F$).[17] Characterization of the monomeric cerium(IV) compounds was explored. Electronic absorption spectroscopy of the amide, alkoxide, and aryloxide complexes showed highly tunable LMCT transitions depending on the ligand environment of the cerium ion. Electrochemical analysis showed that the alkoxide complex was most strongly stabilized in the cerium(IV) oxidation state and that the aryloxide complex was the least stabilized member of the series. DFT assessment of the electronic structures showed minimal metal–ligand overlap and no correlation between the degree of ionicity of the metal–ligand bonds and the cerium(IV/III) redox potential. This work provides a basis for the future design of molecular complexes with purposefully tuned cerium(III/IV) redox potentials and charge transfer transitions.

Exploration of Cerium Redox Chemistry in Aryloxide Complexes with the Use of Pendant Amines has been explored. We have prepared a series of lanthanum and cerium aryl oxide complexes with the formula $K[Ce(OAr)(bdmmp)_3]$ ($Ar = -C_6H_5$ ($-Ph$), $-C_{10}H_7$ ($-Naph$), $-2,4'-Bu-C_6H_3$ ($-dtbp$) and $-2,6-Ph-C_6H_3$ ($-dpp$)) and $K[Ce(OAr)_2(bdmmp)_2]$ ($Ar = -2,6-iPr-C_6H_3$ ($-dipp$)) ($bdmmp = (bis(dimethylamino)methyl-4-phenolate)$ through either metathesis or protonolysis reactions. Cyclic voltammetry was measured for the complexes and found that tetravalent cerium cation was stabilized due to the coordination of electron rich aryloxide ligands.[32] Within the series of complexes, a correlation of electron transfer rates with solid state structures and aryloxide steric encumbrances, qualitatively judged by the peak to peak cathodic and anodic wave separations, was not evident in the series of complexes. We conclude that further work with subtler axial ligand steric variations will be required to elucidate the impact on cerium electron transfer rates.

References:

1. Bogart, J.A., C.A. Lippincott, P.J. Carroll, and E.J. Schelter, *An Operationally Simple Method for Separating the Rare-Earth Elements Neodymium and Dysprosium*. *Angew. Chem. Int. Ed.*, 8222-8225, **2015**.
2. Bogart, J.A., B.E. Cole, M.A. Boreen, C.A. Lippincott, B.C. Manor, P.J. Carroll, and E.J. Schelter, *Accomplishing Simple, Solubility-Based Separations of Rare Earth Elements with Complexes Bearing Size-Sensitive Molecular Apertures*. *Proc. Natl. Acad. Sci. U.S.A.*, 113, 14887-14892, **2016**.
3. Mahoney, B.D., N.A. Piro, P.J. Carroll, and E.J. Schelter, *Synthesis, Electrochemistry, and Reactivity of Cerium(III/IV) Methylene-Bis-Phenolate Complexes*. *Inorg. Chem.*, 52, 5970-5977, **2013**.
4. Behrle, A.C., J.R. Levin, J.E. Kim, J.M. Drewett, C.L. Barnes, E.J. Schelter, and J.R. Walensky, *Stabilization of $M^{IV} = Ti, Zr, Hf, Ce$, and Th Using a Selenium Bis(Phenolate) Ligand*. *Dalton Trans.*, 44, 2693-2702, **2015**.

5. Bogart, J.A., H.B. Lee, M.A. Boreen, M. Jun, and E.J. Schelter, *Fine-Tuning the Oxidative Ability of Persistent Radicals: Electrochemical and Computational Studies of Substituted 2-Pyridylhydroxylamines*. *J. Org. Chem.*, **78**, 6344-6349, **2013**.
6. Bogart, J.A., A.J. Lewis, S.A. Medling, N.A. Piro, P.J. Carroll, C.H. Booth, and E.J. Schelter, *Homoleptic Cerium(III) and Cerium(IV) Nitroxide Complexes: Significant Stabilization of the 4+ Oxidation State*. *Inorg. Chem.*, **52**, 11600-11607, **2013**.
7. Bogart, J.A., A.J. Lewis, M.A. Boreen, H.B. Lee, S.A. Medling, P.J. Carroll, C.H. Booth, and E.J. Schelter, *A Ligand Field Series for the 4f-Block from Experimental and DFT Computed Ce(IV/III) Electrochemical Potentials*. *Inorg. Chem.*, **54**, 2830-2837, **2015**.
8. Kim, J.E., P.J. Carroll, and E.J. Schelter, *Bidentate Nitroxide Ligands Stable toward Oxidative Redox Cycling and Their Complexes with Cerium and Lanthanum*. *Chem. Commun.*, **51**, 15047-15050, **2015**.
9. Kim, J.E., J.A. Bogart, P.J. Carroll, and E.J. Schelter, *Rare Earth Metal Complexes of Bidentate Nitroxide Ligands: Synthesis and Electrochemistry*. *Inorg. Chem.*, **55**, 775-784, **2016**.
10. Bogart, J.A., C.A. Lippincott, P.J. Carroll, C.H. Booth, and E.J. Schelter, *Controlled Redox Chemistry at Cerium within a Tripodal Nitroxide Ligand Framework*. *Chemistry – A European Journal*, **21**, 17850-17859, **2015**.
11. Lee, H.B., J.A. Bogart, P.J. Carroll, and E.J. Schelter, *Structural and Electrochemical Characterization of a Cerium(IV) Hydroxamate Complex: Implications for the Beneficiation of Light Rare Earth Ores*. *Chem. Commun.*, **50**, 5361-5363, **2014**.
12. Piro, N.A., J.R. Robinson, P.J. Walsh, and E.J. Schelter, *The Electrochemical Behavior of Cerium(III/IV) Complexes: Thermodynamics, Kinetics and Applications in Synthesis*. *Coord. Chem. Rev.*, **260**, 21-36, **2014**.
13. Anderson, N.H., S.O. Odoh, U.J. Williams, A.J. Lewis, G.L. Wagner, J. Lezama Pacheco, S.A. Kozimor, L. Gagliardi, E.J. Schelter, and S.C. Bart, *Investigation of the Electronic Ground States for a Reduced Pyridine(Diimine) Uranium Series: Evidence for a Ligand Tetraanion Stabilized by a Uranium Dimer*. *J. Am. Chem. Soc.*, **137**, 4690-4700, **2015**.
14. Pattenaude, S.A., C.S. Kuehner, W.L. Dorfner, E.J. Schelter, P.E. Fanwick, and S.C. Bart, *Spectroscopic and Structural Elucidation of Uranium Dioxophenoxazine Complexes*. *Inorg. Chem.*, **54**, 6520-6527, **2015**.
15. Williams, U.J., J.R. Robinson, A.J. Lewis, P.J. Carroll, P.J. Walsh, and E.J. Schelter, *Synthesis, Bonding, and Reactivity of a Cerium(IV) Fluoride Complex*. *Inorg. Chem.*, **53**, 27-29, **2014**.
16. Williams, U.J., P.J. Carroll, and E.J. Schelter, *Synthesis and Analysis of a Family of Cerium(IV) Halide and Pseudohalide Compounds*. *Inorg. Chem.*, **53**, 6338-6345, **2014**.
17. Williams, U.J., D. Schneider, W.L. Dorfner, C. Maichle-Mossmer, P.J. Carroll, R. Anwander, and E.J. Schelter, *Variation of Electronic Transitions and Reduction Potentials of Cerium(IV) Complexes*. *Dalton Trans.*, **43**, 16197-16206, **2014**.
18. Dorfner, W.L., P.J. Carroll, and E.J. Schelter, *A Homoleptic η_2 Hydroxylaminato Ce^{IV} Complex with S₄ Symmetry*. *Dalton Trans.*, **43**, 6300-6303, **2014**.
19. Levin, J.R., W.L. Dorfner, P.J. Carroll, and E.J. Schelter, *Control of Cerium Oxidation State through Metal Complex Secondary Structures*. *Chem. Sci.*, **6**, 6925-6934, **2015**.

20. Levin, J.R., T. Cheisson, P.J. Carroll, and E.J. Schelter, *Accessing Relatively Electron Poor Cerium(IV) Hydrazido Complexes by Lithium Cation Promoted Ligand Reduction*. *Dalton Trans.*, **45**, 15249-15258, **2016**.

21. Silver, M.A., W.L. Dorfner, S.K. Cary, J.N. Cross, J. Lin, E.J. Schelter, and T.E. Albrecht-Schmitt, *Why Is Uranyl Formohydroxamate Red?* *Inorg. Chem.*, **54**, 5280-5284, **2015**.

22. Anderson, N.H., H. Yin, J.J. Kiernicki, P.E. Fanwick, E.J. Schelter, and S.C. Bart, *Investigation of Uranium Tris(Imido) Complexes: Synthesis, Characterization, and Reduction Chemistry of [U(Ndipp)3(Thf)3]*. *Angew. Chem. Int. Ed.*, **54**, 9386-9389, **2015**.

23. Cary, S.K., M.A. Silver, G. Liu, J.C. Wang, J.A. Bogart, J.T. Stritzinger, A.A. Arico, K. Hanson, E.J. Schelter, and T.E. Albrecht-Schmitt, *Spontaneous Partitioning of Californium from Curium: Curious Cases from the Crystallization of Curium Coordination Complexes*. *Inorg. Chem.*, **54**, 11399-11404, **2015**.

24. Boreen, M.A., J.A. Bogart, P.J. Carroll, and E.J. Schelter, *Rearrangement in a Tripodal Nitroxide Ligand to Modulate the Reactivity of a Ti-F Bond*. *Inorg. Chem.*, **54**, 9588-9593, **2015**.

25. Poitras, A.M., J.A. Bogart, B.E. Cole, P.J. Carroll, E.J. Schelter, and C.R. Graves, *Synthesis and Characterization of Aluminum Complexes of Redox-Active Pyridyl Nitroxide Ligands*. *Inorg. Chem.*, **54**, 10901-10908, **2015**.

26. Herb, T.M., A.M. Poitras, K.G. Richardson, B.E. Cole, J.A. Bogart, P.J. Carroll, E.J. Schelter, and C.R. Graves, *Synthesis and Characterization of Aluminum Nitroxide Complexes*. *Polyhedron*, **114**, 194-199, **2016**.

27. Yin, H., A.J. Lewis, P. Carroll, and E.J. Schelter, *Electrophilic Ln(III) Cations Protected by C-F → Ln Interactions and Their Coordination Chemistry with Weak σ- and π-Donors*. *Inorg. Chem.*, **52**, 8234-8243, **2013**.

28. Yin, H., P.J. Carroll, and E.J. Schelter, *Reactions of a Cerium(III) Amide with Heteroallenes: Insertion, Silyl-Migration and De-Insertion*. *Chem. Commun.*, **52**, 9813-9816, **2016**.

29. Yin, H., J.R. Robinson, P.J. Carroll, P.J. Walsh, and E.J. Schelter, *[Small Kappa]2-Coordination of 18-Crown-6 to Ce(III) Cations: Solution Dynamics and Reactivity*. *Chem. Commun.*, **50**, 3470-3472, **2014**.

30. Yin, H., A.V. Zabula, and E.J. Schelter, *C-F → Ln/An Interactions in Synthetic F-Element Chemistry*. *Dalton Trans.*, **45**, 6313-6323, **2016**.

31. Yin, H., P.J. Carroll, and E.J. Schelter, *Cerium(III) and Uranium(IV) Complexes of the 2-Fluorophenyl Trimethylsilyl Amide Ligand: C-F → Ln/An Interactions That Modulate the Coordination Spheres of F-Block Elements*. *Inorg. Chem.*, **55**, 5684-5692, **2016**.

32. Kim, J.E., P.J. Carroll, and E.J. Schelter, *Structural Variation in Cerium Aryloxide Complexes Templated by Hemilabile K+-Amine Interactions*. *New J. Chem.*, **39**, 6076-6084, **2015**.